

Double nuclear coherence transfer (DONUT)-HYSCORE: A new tool for the assignment of nuclear frequencies in pulsed EPr experiments

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Abstract

A two-dimensional experiment, termed DONUT-HYSCORE (double nuclear coherence transfer hyperfine sublevel correlation) designed to obtain correlations between nuclear frequencies belonging to the same electron spin manifold is presented. The sequence employed is $\pi/2$ - τ - $\pi/2$ - t_1 - π - τ_2 - π - t_2 - $\pi/2$ - τ_1 -echo, and the echo is measured as a function of t_1 and t_2 whereas τ_1 and τ_2 are held constant. It is complementary to the standard HYSCORE experiment which generates correlations between nuclear frequencies belonging to different $M(s)$ manifolds and is particularly useful for ^{14}N nuclei. The experiment is first demonstrated on a single crystal of copper-doped L-histidine hydrochloride monohydrate where the modulations are induced by a single ^{14}N nucleus, the remote nitrogen in the imidazole group. HYSCORE and DONUT-HYSCORE experiments were carried out on two crystal orientations. In the first, one Cu^{2+} site contributes to the echo and all six nuclear frequencies together with the expected correlation were observed. In the second, 12 frequencies corresponding to two Cu^{2+} ions at different crystallographic sites appeared and all expected correlations were detected as well. This rather trivial example demonstrates that the DONUT-HYSCORE pulse sequence indeed generates correlations within the $M(s)$ manifolds. The value of the DONUT-HYSCORE experiment is demonstrated on a frozen solution of a vanadyl complex with a bis-hydroxamate ion binder (VO-RL515). The modulations in this complex arise from the two InN nuclei in the hydroxamate groups, and orientation-selective three-pulse ESEEM (electron spin-echo envelope modulation) spectra showed a number of well-resolved peaks. An unambiguous assignment of all peaks and their orientation dependences could not be achieved through HYSCORE alone because at certain orientations frequencies of one of the $M(s)$ manifolds were absent or overlapped with those of the other manifold. The application of the DONUT-HYSCORE experiment provided new correlations that led to the complete assignment of the ESEEM frequencies, thus paving the way for future systematic spectral simulations for the determination of the best-fit Hamiltonian parameters. This example shows that, in the case that the HYSCORE experiment cannot distinguish between two sets of frequencies belonging to the same $M(s)$ manifold in different centers (or orientations) because signals from the other manifold are missing or overlapping, the DONUT-HYSCORE becomes most valuable.

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